



Unlocking efficient and robust ozone decomposition with CNT-confined manganese oxide via synergistic electronic modulation

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ABSTRACT

Manganese oxides (MnO₂)-based catalysts are prominent candidates for ozone elimination, which always bear the accumulation of the intermediate oxygen species and water, resulting in unsatisfactory catalytic efficiency. To overcome this critical defect, we propose carbon nanotubes confined MnO₂ catalysts (MnO₂-in-CNT) for efficient and stable ozone decomposition over a wide relative humidity range (RH, 15–90%). Strikingly, the catalyst exhibits an efficient and sustainable ozone conversion (98%) over 100 h under a gas hourly space velocity (GHSV) of 600,000 mL g⁻¹ h⁻¹ and RH of 15%, and durability under high RH (77% over 50 h, RH 70%), well beyond its unconfined analog and most reported works. This excellent catalytic performance can be attributed to the facilitated intermediate desorption on active sites and the confined structure alleviated the effect of water on inner MnO₂. This discovery is expected to drive great progress in the applications of confined-structure catalysts for air purification.

1. Introduction

Ground-level ozone, as a highly toxic gas, has become one of the major airborne pollutants [1,2]. Ozone is primarily derived from the photochemical reactions between nitrogen oxides (NO_x) and volatile organic compounds (VOCs), or the emissions from the modern household equipment, such as photocopiers and ultraviolet disinfection [3,4]. It is known that long-term exposure to ozone, even at low concentration levels (>100 ppb), is detrimental to both the ecosystems and human health [5–7]. Therefore, it is urgent to develop the safe, efficient and economical ozone elimination methods.

Currently, heterogeneous catalytic decomposition is the most promising method due to its higher efficiency, lower cost, as well as feasibility at room temperature attracting considerable attention [8]. Among various catalysts, manganese oxides (MnO₂) have been deemed as the most active catalysts for the ozone elimination among diversified transition metal oxide catalysts [9–12]. In addition, a conventional catalytic ozone decomposition process over manganese-based catalysts proceeds by the following equations:



where R corresponds to the reaction rate, $*$ means the active site, P_{O_3} represents the ozone partial pressure, θ refers to the fraction of total active sites, and k denotes the constant. In general, the rate (R) of step (1) is much faster than that of step (2) and step (3), with the slowest step (3) becomes the rate-determining step [13,14]. Under the identical P_{O_3} , the rate of all the steps depends on the fraction of total active sites (θ) available to react with the reactants (Eqs. 1–3). The slow desorption of the peroxide species to gaseous oxygen during the step (3) results in the accumulation of peroxide species at the active sites of the catalyst, thus decreasing the overall efficiency of the ozone decomposition [14,15]. The accumulation of the surface peroxide and the water-induced deactivation remain two crucial obstacles for the practical application of the manganese-based catalysts in the ozone decomposition.

In fact, great efforts have been made to overcome these two challenges [16–18]. For example, Zhang et al. utilized the synergy effect of Mn and Co in (Mn, Co)₃O₄ to accelerate the rate-determining steps [14]. Besides, Zhu et al. encapsulated the α -MnO₂ nanofiber with the hydrophobic graphene shells to hinder the chemisorption of water vapour, thereby enhancing its water resistance [19]. Although the reported methods improved the decomposition performance and the water tolerance to a certain extent, the catalytic performance still remains to be boosted further. Therefore, there is a great environmental and

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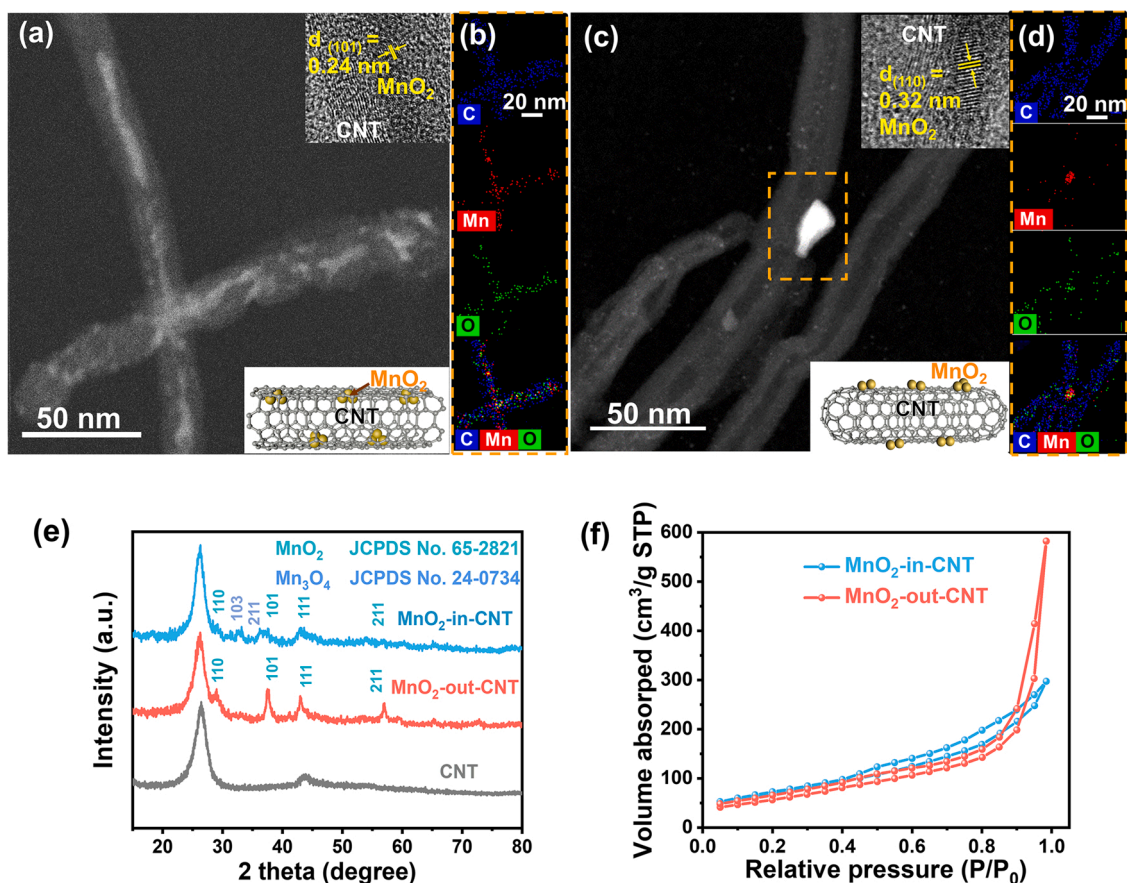


Fig. 1. HADDF-STEM image, (Insets) HRTEM images and element mapping images of (a, b) MnO_2 -in-CNT and (c, d) MnO_2 -out-CNT. (e) XRD patterns of CNT, MnO_2 -in-CNT and MnO_2 -out-CNT. (f) N_2 adsorption-desorption isotherms of MnO_2 -in-CNT and MnO_2 -out-CNT.

economic demand to develop cost-effective catalytic materials with high activity, strong stability and excellent humidity resistance.

The confinement of the catalytic center inside the nanoscale space, as is reported, could lead to unique intermolecular arrangements that lower the activation energy barrier and alter the stability of certain reactions, which have significant effects on the catalytic performance [20–22]. A variety of different types of confined-structure catalysts (such as the nanopores or nanoholes in porous architectures [23], the nanochannels in tubular structures [24], as well as the van der Waals gaps in layered materials [25]) have been exploited. Among them, carbon nanotubes (CNTs) have well-defined hollow interiors and exhibit outstanding mechanical as well as electron conductivity [26,27]. Recently, special attention has been directed to CNT-confined catalysts owing to the catalytic reaction benefits significantly from proceeding within a nano-sized CNTs reaction vessel, where the activity and stability exceed that on the outside of the nanotubes by more than an order of magnitude [27–29]. Inspired by this, it might be reasonable to expect that the encapsulation of the manganese-based catalysts into the CNT cavities can show greater redox activity and stability. However, the performance of the confined-structure catalysts on the catalytic ozone decomposition still remains elusive.

On this view, we herein take a confined-structure catalyst that encapsulated the MnO_2 nanoparticles into CNT (MnO_2 -in-CNT) to improve the activity and stability of the ozone decomposition in a wide humidity range. As expected, the catalyst exhibited ultra-high catalytic stability over a wide humidity range (15 ~ 90%). Under a gas hourly space velocity (GHSV) of $600,000 \text{ mL g}^{-1} \text{ h}^{-1}$ and relative humidity (RH) of 15%, the ozone conversion efficiency was as high as 98% over 100 h, showing excellent stability. Even though the RH increased to 70%, the ozone conversion also reached up to 77% over 50 h, far

exceeding its unconfined analog (MnO_2 -out-CNT and bare MnO_2) and the most reported works. Furthermore, this cost-effective system can simultaneously decompose O_3 and VOCs, thus realizing the air purification. Combining FTIR, XPS results and density functional theory (DFT) calculations, it is observed that the ozone decomposition over MnO_2 -in-CNT occurs not only the surface of the MnO_2 in the confined space, but also on the nearby exterior surface of CNT, due to the changed surface electronic properties through the interfacial electron modulation. The barrier of the rate-determining steps (peroxides desorption) in MnO_2 -in-CNT is significantly lower than those of the single MnO_2 . Additionally, the confined structure protected the active sites on the inner MnO_2 against the water-induced deactivation and the catalyst deterioration during the ozone decomposition.

2. Experimental section

2.1. Synthesis of MnO_2 -in-CNT and MnO_2 -out-CNT

Synthesis of MnO_2 -in-CNT membrane: Raw CNT was firstly refluxed in HNO_3 (68 wt%) at 130°C for 12 h [30]. The resulting CNT was functionalized with carbonyl groups with open ends. After being filtered and washed with ultrapure water until neutral pH, the products were lyophilized. Afterwards, $134 \mu\text{L}$ of $\text{Mn}(\text{NO}_3)_2$ (50 wt%) was dissolved in 3.2 mL ethanol and then added dropwise to 200 mg of the pre-treated CNT. The mixed solution was treated by ultrasonication for 1 h, then stirred for 4 h, and dried at room temperature. The obtained products were gradually heated to 300°C in air and kept for 2 h. The obtained sample is denoted as MnO_2 -in-CNT. Subsequently, the sample was dispersed in ethanol (0.1 g sample / 3 mL ethanol) and dropwisely coated onto a commercial poly tetra fluoroethylene (PTFE) filter

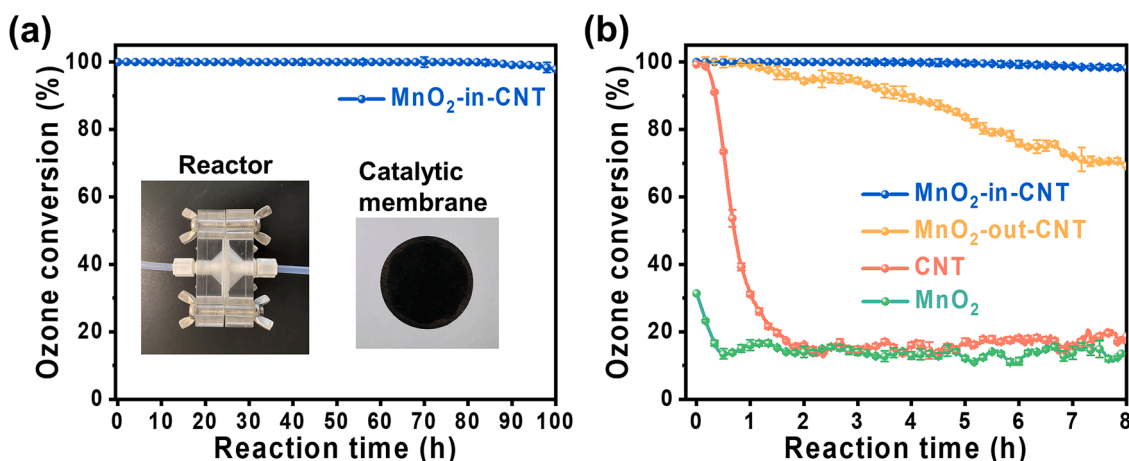


Fig. 2. (a) Ozone conversion of the supported catalyst. Inset: Photo of MnO₂-in-CNT loaded on the PTFE membrane, (b) Ozone conversion performance of samples under 15% RH.

membrane (D = 47 mm, pore size = 5 μm) to obtain the catalytic membrane.

Synthesis of MnO₂-out-CNT membrane: For MnO₂-out-CNT sample, CNT with closed caps was used, which were obtained by refluxing raw CNT in HNO₃ (37 wt%) solution at 110 $^{\circ}\text{C}$ for 5 h. Afterwards, MnO₂ deposited on the close capped CNT was prepared and loaded onto porous PTFE membrane under the identical procedures as MnO₂-in-CNT. The obtained sample was labeled as MnO₂-out-CNT membrane.

2.2. Catalytic activity tests

The catalytic activity for the ozone decomposition was evaluated at room temperature (25 $^{\circ}\text{C}$) in a continuous flow membrane reactor with the as-prepared catalytic membrane fixed in the catalytic membrane reactor by O-rings (Fig. S1a and b). O₃ was generated from an ozone generator (CH-ZTW3G, China) with clean air as oxygen source. During reaction, the O₃ gas continuously passed through the catalytic membrane reactor. The RH was adjusted by passing compressed dry N₂ through a constant water bath bubbler to mix with the O₃ gas, the value of RH was measured by a hygrometer (Elitech, GSP-6, China). The total gas flow was kept at 1000 mL min⁻¹, and the inlet O₃ concentration was kept at 50 ppm. The inlet and outlet O₃ concentration was detected by an O₃ detector (model 106-L, 2B Technologies). The conversion of ozone was calculated using the following equation:

$$\text{O}_3 \text{ removal rate} = (C_{\text{in}} - C_{\text{out}}) / C_{\text{in}} \times 100\% \quad (4)$$

where C_{in} and C_{out} are inlet and outlet concentrations of O₃, respectively.

3. Results and discussion

3.1. Characterization of MnO₂-in-CNT

We respectively deposited MnO₂ nanoparticles inside and outside of the CNTs, denoted as MnO₂-in-CNT and MnO₂-out-CNT as catalysts for ozone removal. The synthesis process of MnO₂-in-CNT and MnO₂-out-CNT is illustrated in Fig. S2. The TEM images (Fig. S4 and S5) and detailed analysis on high-angle annular dark-field mode (HAADF) STEM (Fig. S6 and Fig. 1) clearly demonstrate the successful confinement of MnO₂ nanoparticles in the tubes (inner diameter of ca. 8 nm) of CNT in MnO₂-in-CNT, while the MnO₂ in MnO₂-out-CNT deposited on the CNT exterior surface. The element mapping result of MnO₂-in-CNT (Fig. 1b) demonstrates the material confined in CNTs is manganese oxide, while its crystallinity was confirmed by powder X-ray diffraction (XRD) (Fig. 1e), high-resolution transmission electron microscopy (HRTEM) images inset (Fig. 1a) and selected area electron diffraction (SAED)

pattern (Fig. S7). The XRD patterns (Fig. 1e and S8) show that both MnO₂-out-CNT and MnO₂-in-CNT exhibit characteristic diffraction peaks of the (002) and (100) crystal planes of CNT (JCPDS No. 65-6212) and diffraction peaks of (110), (101), (111), (211) corresponding to β -MnO₂ (JCPDS No. 65-2821), the weak peaks at 32.4 $^{\circ}$ and 36.1 $^{\circ}$ assigned to (103) and (211) planes of Mn₃O₄ (JCPDS No. 24-0734) were also detected. The results indicate that slight amount of reduced oxide-Mn₃O₄ coexists in the sample MnO₂-in-CNT, attributing to the strong interaction between encapsulated MnO₂ and interior wall of CNT walls [30,31]. The (002) plane of CNT and the (101) plane of MnO₂ were observed in HRTEM results. The Raman spectra of MnO₂-in-CNT and MnO₂-out-CNT show two bands centered at 1584 cm⁻¹ and 1356 cm⁻¹ (Fig. S9), corresponding to the characteristic E_{2g} and D modes of carbon nanotubes, respectively [32]. The Raman band centered at 637 cm⁻¹ is attributed to the Mn-O bond vibrations [33]. However, for MnO₂-in-CNT, the Mn-O band is weaker, which may be due to the encapsule of the MnO₂ in CNT [19].

The weight percentage of MnO₂ and CNTs in MnO₂-in-CNT and MnO₂-out-CNT were analyzed by TG-DSC (Fig. S10). It is calculated that the amount of MnO₂ in both MnO₂-in-CNT and MnO₂-out-CNT samples was ca. 24 wt%, corresponding to the Mn/C molar ratio of 1:23. The accurate content of Mn in the MnO₂-in-CNT and MnO₂-out-CNT was determined to be 15.5% and 15.1%, respectively, revealing the MnO₂ ratio is ca. 0.245 wt% and 23.9 wt%. The results were in good agreement with the experimental results of TG-DSC. The N₂ adsorption-desorption isotherms are shown in Fig. 1f, the MnO₂-in-CNT exhibits higher surface area ($S_{\text{BET}} = 250.374 \text{ m}^2 \text{ g}^{-1}$) and narrower pore volume ($0.428 \text{ cm}^3 \text{ g}^{-1}$) than that of MnO₂-out-CNT ($S_{\text{BET}} = 212.549 \text{ m}^2 \text{ g}^{-1}$, $0.859 \text{ cm}^3 \text{ g}^{-1}$) due to the open-capped CNT and the MnO₂ accommodate inside the channels of CNTs in MnO₂-in-CNT. The element states of samples were analyzed by X-ray photoelectron spectroscopy (XPS). The Mn 2p_{2/3} peak of MnO₂-in-CNT and MnO₂-out-CNT can be deconvoluted into three peaks with the binding energy at 641.6, 642.6 and 643.6 eV, corresponding to Mn²⁺, Mn³⁺ and Mn⁴⁺, indicating the multiple valence states of Mn (Fig. S11). Furthermore, the structure and surface component of MnO₂-in-CNT (Fig. S12) and MnO₂-out-CNT (Fig. S13) catalyst after long-term reaction were examined by XRD and XPS (Mn 2p). As shown in Fig. S12, there was no significant variation before and after the reaction, indicating the excellent stability of MnO₂-in-CNT.

3.2. Ozone catalytic activity

To ascertain the effect of the confinement on ozone decomposition. A continuous-flow membrane reactor is used to evaluate the catalytic performance of ozone decomposition ($\text{GHSV} = 600,000 \text{ mL g}^{-1} \text{ h}^{-1}$) at

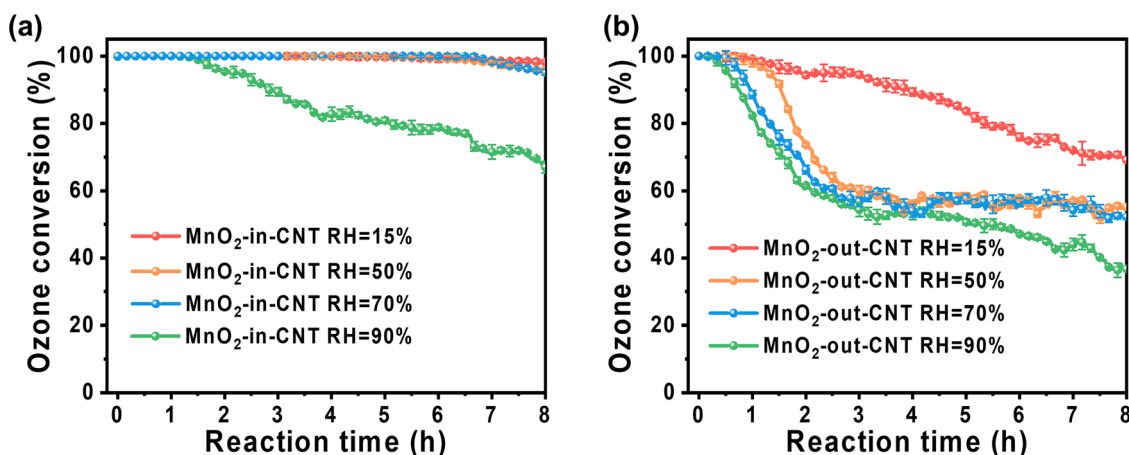


Fig. 3. Ozone conversion on (a) MnO_2 -in-CNT and (b) MnO_2 -out-CNT under different humidity conditions.

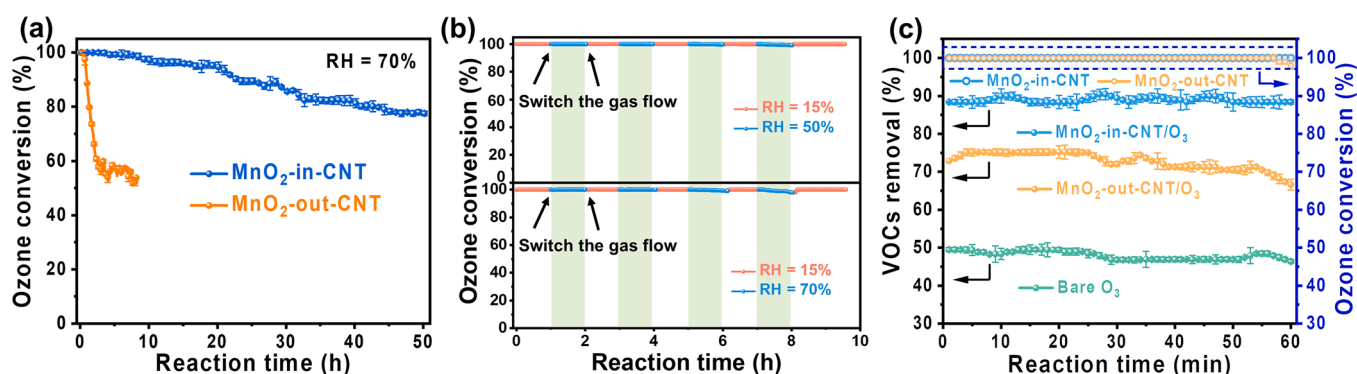


Fig. 4. (a) Ozone conversion performance of MnO_2 -in-CNT and MnO_2 -out-CNT under 70% RH. (b) Ozone conversion performance on MnO_2 -in-CNT at alternate relative humidity (15% RH and 50% RH, 15% RH and 70% RH). (c) Simultaneous removal of VOCs and O_3 in different system.

ambient temperature. We optimized the MnO_2 -in-CNT by adjusting the MnO_2 loading amount from 10 to 30 wt% (Fig. S14). MnO_2 -in-CNT with an optimal MnO_2 loading amount of ca. 20 wt% was used in the following reaction system. As shown in Fig. 2a, the MnO_2 -in-CNT catalyst exhibits 98% persistent ozone conversion efficiency and excellent stability over 100 h under RH of 15%. However, the ozone conversion on MnO_2 -out-CNT catalyst sharply decrease to only 70% after 8 h (Fig. 2b), which could be due to the accumulation of intermediate oxygen species on MnO_2 -out-CNT. The result reveals the remarkable enhanced activity of the MnO_2 particles inside compared with those deposit outside the CNT. The bare MnO_2 sample gives only an ozone conversion below 20% after 8 h. Although the CNT shows good initial catalytic activity (100%), the conversion rate dramatically drops to 17% at 1 h, which might be ascribed to the adsorption saturation of O_3 [34, 35].

Nevertheless, manganese-based catalysts inevitably suffered serious deactivation under humid ozone atmosphere due to the poisoning of water molecules [11,36,37]. Therefore, the ozone decomposition performance under high-humidity conditions was explored. As shown in Fig. 3, MnO_2 -in-CNT achieved nearly 100% ozone decomposition efficiency both at 15%, 50%, and 70% RH after 8 h, and the efficiency remained stable even after continuous reaction at 70% RH for 50 h (Fig. 4a), while the ozone conversion on MnO_2 -out-CNT decreased drastically from 70% to 55% and 52% under RH of 15–50%, and 70%. Moreover, the ozone conversion ratio of MnO_2 -in-CNT can be stabilized at 100% under the humidity recycle from 50% to 15% and from 70% to 15%. Even when the humidity decreases from 90% to 15%, the ozone conversion efficiency of MnO_2 -in-CNT can still be quickly recovered to 100% (Fig. 4b and S16), which suggests the regeneration can easily

occur under alternate humidity conditions reveals the weak adsorption of H_2O on the MnO_2 -in-CNT. The H_2O -TPD was further investigated to identify the H_2O adsorption on the catalyst surface. As shown in Fig. S17, compared with MnO_2 -out-CNT and MnO_2 , the MnO_2 -in-CNT demonstrates the lower adsorption capacity of water, indicating the adsorption of water is hindered on MnO_2 -in-CNT. And the FTIR spectra of samples at dry and humidity were investigated (Fig. S18), the peak of adsorbed water (3464 cm^{-1}) on samples were enhanced under moisture, but the weaker changes in the MnO_2 -in-CNT sample was observed, which further indicates that the adsorption of water is hindered on MnO_2 -in-CNT. CNT hosts may act as nanoreactors to decrease the direct contact of interior MnO_2 with water vapor. These results collectively the CNT framework alleviates the effect of water vapour on the ozone conversion on MnO_2 -in-CNT and also makes catalyst regeneration much easier. The ozone decomposition performance in terms of O_3 conversion, GHSV, RH and reaction time in our system was compared to that in other works reported in the literature (Table S1 and S2). Notably, the MnO_2 -in-CNT offers long-term durability and water tolerance that exceed most reported studies.

To further highlight the potential of MnO_2 -in-CNT catalyst for the air purification, we carried out the simultaneous catalytic destruction of VOCs (CH_3SH) and ozone, which had an original CH_3SH of 40 ppm and ozone of 50 ppm. As shown in Fig. 4d, the MnO_2 -in-CNT achieved highly stable removal efficiency (90% for 40 ppm of CH_3SH and 100% for 50 ppm of O_3) under a GHSV of $120,000\text{ mL h}^{-1}\text{ g}^{-1}$, obviously beyond the MnO_2 -out-CNT catalyst (67% for CH_3SH and 98% for O_3) and ozone alone (46% for CH_3SH), indicating the high activity of MnO_2 -in-CNT to simultaneously eliminate VOCs and ozone under ambient temperature. The above experimental results reveal MnO_2 -in-CNT catalyst possesses

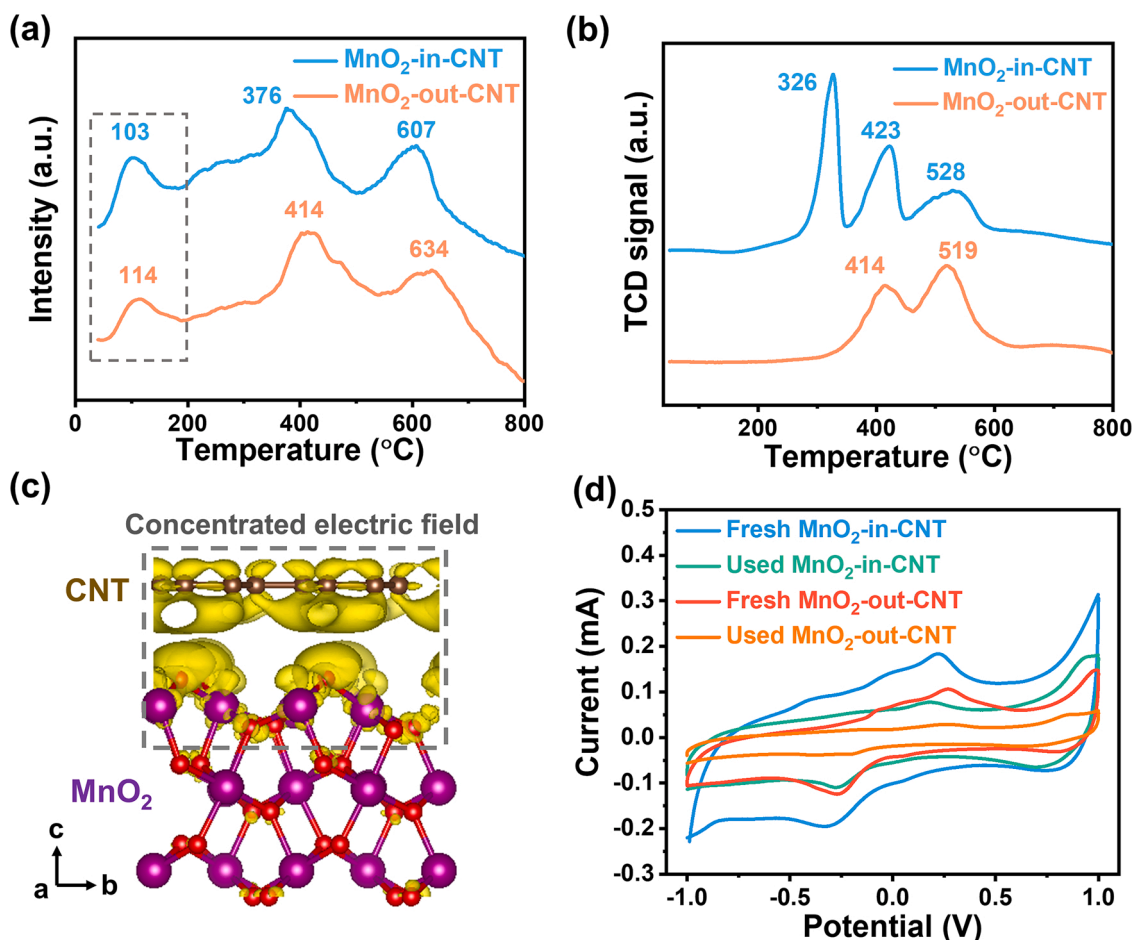


Fig. 5. (a) O₂-TPD profiles and (b) H₂-TPR profiles of MnO₂-in-CNT and MnO₂-out-CNT. (c) Charge density difference diagrams of MnO₂-in-CNT. (d) CV curves of fresh and used MnO₂-in-CNT and MnO₂-out-CNT.

an efficient and robust redox activity, and outstanding water tolerance that shows promising application potential toward ozone elimination, as well as great potential for purification of complex air pollution.

3.3. Identification of active sites

Identification of the active sites is essential for understanding the catalytic behavior. Hence, we conducted the O₂ temperature programming desorption (O₂-TPD), H₂ temperature programmed reduction experiments (H₂-TPR), DFT calculations, and Cyclic voltammetry (CV) to observe the active sites and redox ability of MnO₂-in-CNT. The mobility of oxygen species in samples was analyzed by O₂-TPD. As shown in Fig. 5a, the peaks at 103 °C of MnO₂-in-CNT can be attributed to the desorption of weak adsorbed oxygens, which can be corresponded to the peroxides desorption from Mn active sites in the step (3) (Eq. 3) [38]. Noteworthy, the MnO₂-in-CNT demonstrates lower oxygen desorption temperature of the oxygen and larger desorption peak area compared to MnO₂-out-CNT, revealing the confined structure compromised the energy barriers of oxygen desorption step, which is greatly helpful for accelerating the rate-determining step (peroxide species desorption, Eq. 3) in ozone decomposition. In the medium-temperature (350–600 °C), the MnO₂-in-CNT sample exhibits lower desorption temperature than MnO₂-out-CNT indicate the higher activity and mobility of lattice oxygen in MnO₂-in-CNT, which is beneficial to the redox reactions [9,39,40]. The results of H₂-TPR are shown in Fig. 5b, three reduction peaks at 326, 423 and 528 °C were observed in MnO₂-in-CNT, which can be assigned to the reduction of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄ and Mn₃O₄ to MnO, respectively [41,42]. The reduction peaks of

MnO₂-out-CNT located at 414 and 519 °C that are higher compared to that of MnO₂-in-CNT, indicating the MnO₂-in-CNT owns stronger reducibility and higher mobility of oxygen species than MnO₂-out-CNT, which is important for the ozonolysis reaction.

The electronic structure within MnO₂-in-CNT was simulated by the charge density difference calculation (Fig. 5c). Interestingly, the charge-density differences demonstrate that most electrons concentrated in the confined space between the inner MnO₂ and interior wall of CNT, with a fraction of electrons accumulate at the exterior wall of the nearby CNT, revealing the electron-rich sites mainly located at the confined space of MnO₂-in-CNT due to confinement effect, and the nearby exterior walls of CNT also can be the active sites. It is reported the electrons can be transferred from the Mn exposure site (oxygen vacancy) to the nearby graphene layer and correspondingly an electron-rich site can be formed at the nearby surface of graphene [19]. Given that the similar properties of graphene and CNT, the electrons of Mn atoms in MnO₂-in-CNT also can be transferred to the nearby exterior walls of CNT. O₃ is an electrophilic molecule, which is readily adsorbed and reacts at sites with high electron density [43]. As shown in the C 1s spectra of XPS of MnO₂-in-CNT (Fig. S19), the peak of C=O and C-O slightly increased after being treated with ozone due to a fraction of the carbon surface of CNT shells were oxidized to C=O groups and COOH groups, revealing the ozonation process also appears on the CNT shells of MnO₂-in-CNT. Furthermore, the electron mobility in the catalysts was evaluated by CV curves. As shown in Fig. 5d, the current of MnO₂-in-CNT is much higher than that of MnO₂-out-CNT, proving the stronger electron transfer ability of MnO₂-in-CNT [44]. It's worth noting that the relatively weaker change in the current intensity of MnO₂-in-CNT after ozone-catalytic

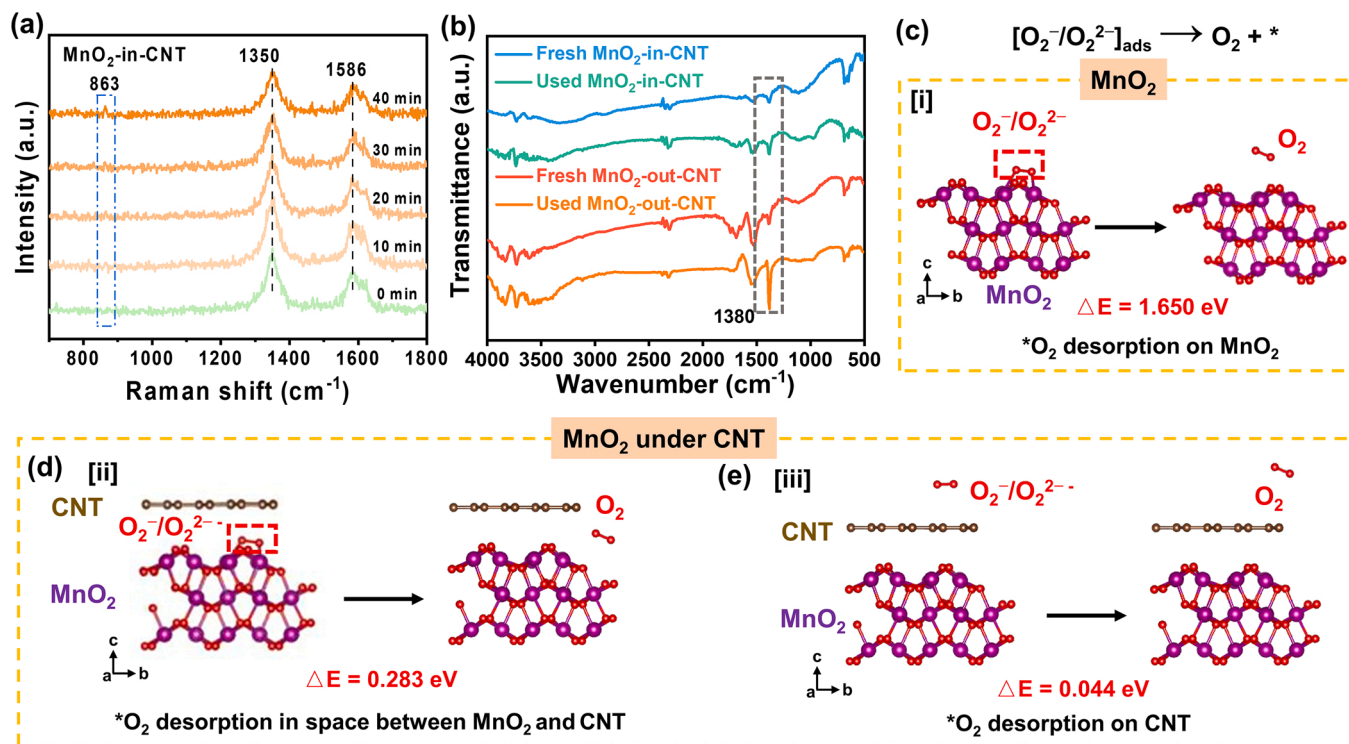


Fig. 6. (a) In situ Raman spectra of MnO_2 -in-CNT with 40 min continuous O_3 flow passing at room temperature (25 °C). (b) FTIR spectra of fresh and used MnO_2 -in-CNT and MnO_2 -out-CNT. (c) O_2^* desorption energy on exposed MnO_2 . (d, e) O_2^* desorption energy on MnO_2 -in-CNT.

reaction compare with that of MnO_2 -out-CNT was demonstrated, indicating the stronger electron compensation ability in MnO_2 -in-CNT which could enhance the long-term catalytic stability. Moreover, it has been reported that the electrons can transfer from the enclosed catalysts to the carbon shells in the confined-structure catalyst and further penetrate through the interior CNT shell to exterior of CNT based on the results of the C K-edge XANES, STXM, and DFT calculation [45]. Hence, the ozone-catalytic decomposition takes place both inside and outside of CNT in MnO_2 -in-CNT. Considering the reaction on CNT shell also can take place on MnO_2 -out-CNT but the significantly poorer catalytic performance than MnO_2 -in-CNT, it can be deduced the surface of MnO_2 in the confined space should be the main active sites in MnO_2 -in-CNT that enhanced the ozone decomposition. The confined configuration provides MnO_2 -in-CNT with a better redox activity, which is crucial for the ozone-catalytic decomposition.

3.4. Ozone conversion mechanism on MnO_2 -in-CNT

Based on the above understanding, reaction intermediates were further analyzed by in situ Raman, FTIR and ESR to explore the ozone reaction mechanism on MnO_2 -in-CNT. As shown in Fig. 6a, with continuous O_3 flow, a new peak was observed at 863 cm^{-1} , which was attributed to peroxide (O_2^{2-}) [18,38]. It is worth noting that the increase of the peak intensity in MnO_2 -in-CNT is weaker than that in MnO_2 -out-CNT (Fig. S20). This indicates that the accumulation of O_2^{2-} is reduced on MnO_2 -in-CNT compared with MnO_2 -out-CNT. In the FTIR spectra (Fig. 6b), the peak at 1380 cm^{-1} associated with the free O_2 [46] can be observed in both MnO_2 -in-CNT and MnO_2 -out-CNT, the surface O_2 comes from the O_2 accumulated on surface that derived from the desorbed peroxide species ($\text{O}_2^* \rightarrow \text{O}_2 + *$). Moreover, the peak intensity of surface O_2 in used MnO_2 -in-CNT is much weaker than that of used MnO_2 -out-CNT, which can also indicate that the desorption of O_2^* on MnO_2 -in-CNT is easier than that of MnO_2 -out-CNT. As shown in Fig. S21, the signal of O_2^* was also detected in the MnO_2 -in-CNT system, where the intensity is higher than that of MnO_2 -out-CNT, relating to O_2^*

transferring electrons to catalyst to release O_2^* . These results confirmed the reduced accumulation of peroxide on MnO_2 -in-CNT compared with unconfined analog.

DFT calculations were used to investigate the energy barrier of rate-determining step (O_2^* desorption) on the catalyst surface (Fig. 6c-e). Based on the results of active sites identification, we monitored the O_2^* desorption process (i) on the single MnO_2 (Fig. 6c), (ii) on the surface of MnO_2 in the confined space (Fig. 6d), and (iii) on the exterior wall of carbon shell in the system of MnO_2 under a carbon shell (Fig. 6e). The calculation results reveal the O_3 molecules are prone to attach on MnO_2 rather than on carbon shell. Moreover, the desorption barrier of O_2^* attached on the exterior wall of a carbon shell (iii) and that in the confined space between MnO_2 and carbon shell (ii) are 0.04 and 0.28 eV, respectively, which is significantly lower than that of O_2^* on exposed MnO_2 (1.7 eV, (i)), and also lower than the reported ozone decomposition catalyst that has realized accelerated O_2^* desorption [38]. In the MnO_2 -in-CNT system, the process (ii) could happen on the surface of MnO_2 in the confine space, and process (iii) could happen on the external wall of the CNT, while (ii) should be the main O_2^* desorption process due to the electronic structure in MnO_2 -in-CNT system. (i) should be the main O_2^* desorption process in the MnO_2 -out-CNT system with a slight proportion of process (iii) happens on CNT due to the higher affinity of O_3 on MnO_2 . O_2^* desorption process in the bare MnO_2 is shown as process (i). These results revealed the weakened bonding of O_2^* in MnO_2 -in-CNT. The stronger electronic interaction between the inner MnO_2 and the interior wall of the CNT modulates its binding energies with O_2^* [47]. Meanwhile, the significantly compromised reaction barrier on the exterior wall of carbon (0.04 eV) could be attributed to the transfer of interfacial electron from Mn atoms to the nearby carbon shell that effectively modifies the surface electronic properties, which gives the catalyst a moderate local work function to facilitate the desorption of the O_2^* [19]. The DFT results coincide well with the results observed by O_2 -TPD, ESR and FTIR, confirming the rate-determining step of peroxide species desorption is easier to occur on MnO_2 -in-CNT, thereafter releasing more available active sites for

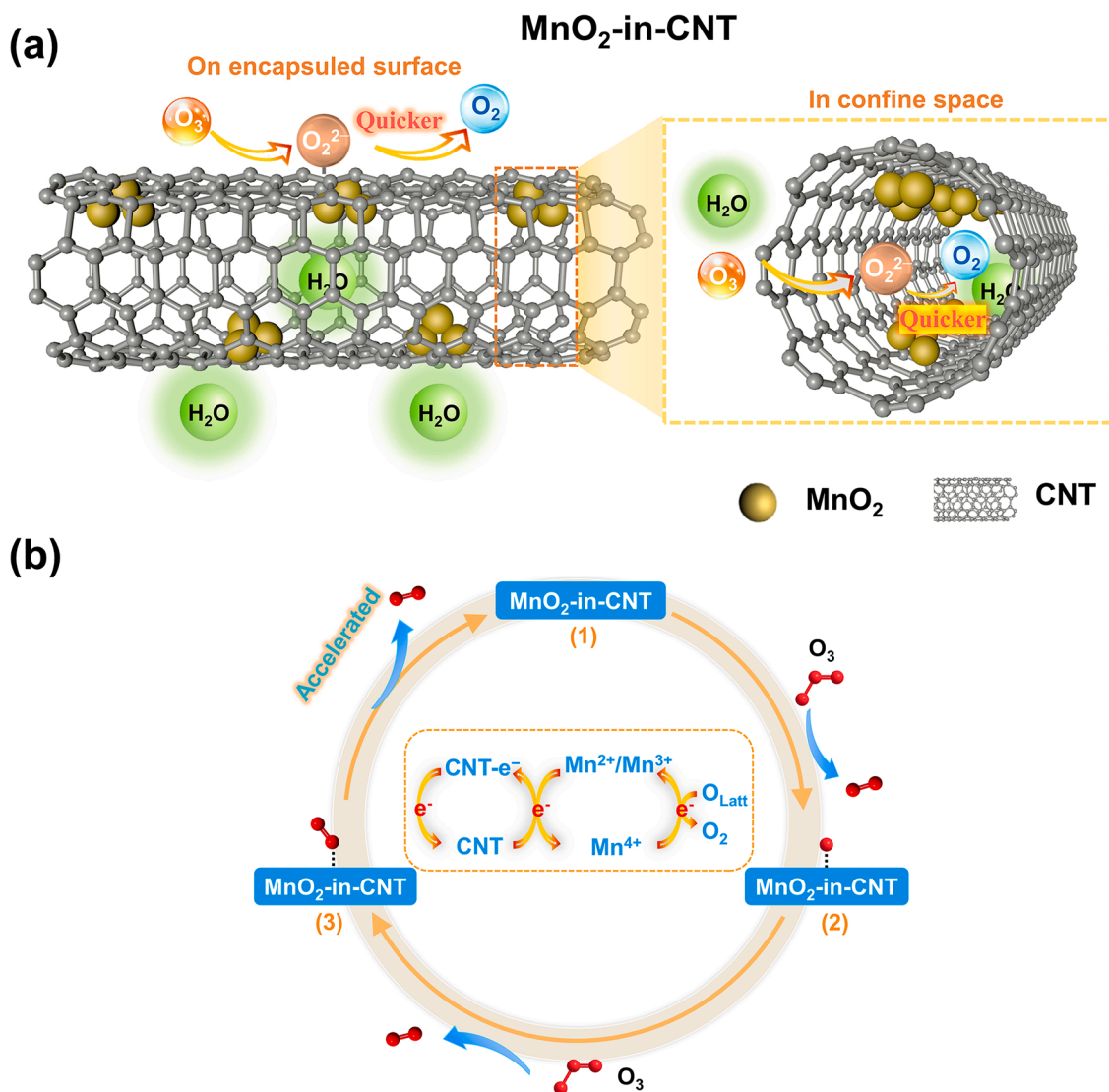


Fig. 7. (a) The schematic diagram of ozone decomposition on MnO₂-in-CNT. (b) The reaction mechanism of ozone decomposition on MnO₂-in-CNT.

accelerating the ozone decomposition and realizing impressive stability in long-term.

According to the above performances and calculations, the ozone decomposition mechanism over the MnO₂-in-CNT system is proposed. As shown in Fig. 7a and Fig. S22, ozone molecules diffuse into the carbon nanotubes of MnO₂-in-CNT and the ozone decomposition over MnO₂-in-CNT on the surface of the MnO₂ in the confined space are the main reactive sites, where the oxygen vacancies in MnO₂ should play the main role [16]. Meanwhile, CNT can be activated by the electron transferred from the nearby Mn atoms, thereby partial ozone molecules attach on the exterior wall of CNT and are catalyzed. As shown in Fig. 7b, ozone molecules are dissociative adsorbed on those active sites and are catalyzed to form oxygen molecules and oxygen species (*O). The *O will continue to react with another ozone molecule to form peroxide species (*O₂). Eventually, the *O₂ desorbed from catalyst to release O₂ and O₂⁻ after transferring electron back to catalyst (Fig. S23 and Table S3), which is the rate-determining step of ozonolysis. This rate-determining step occurs more easily on MnO₂-in-CNT compared to MnO₂ attributing to the confined-structure merits. Meanwhile, confinement of MnO₂ within CNTs greatly decreased the direct contact of interior MnO₂ with water vapor, enabling the MnO₂-in-CNT catalyst to maintain an efficient and robust ozone decomposition performance under high humidity.

4. Conclusion

Our work has presented a space-confined catalyst using interface electronic modulation (MnO₂-in-CNT) to achieve exceptional ozone decomposition activity, impressive stability in long-term and moisture suitability, and provided a mechanistic understanding of the confined-structure merits on ozone decomposition. Moreover, this confinement system can also simultaneously decompose O₃ and VOCs to achieve air purification. Combining experimental characterizations and DFT calculations, it is observed that the ozone decomposition on MnO₂-in-CNT exhibited undermined barriers of rate-determining step of ozone decomposition. Meanwhile, the confined structure alleviated the effect of water vapor on ozone conversion. This cost-effective system with high activity, impressive stability and humidity tolerance is expected can be applied to reduce ground-level ozone. We hope our work could stimulate the researchers to develop efficient dimensionally confined catalysts for various air pollution applications to improve the atmospheric environment.

CRediT authorship contribution statement

Bin Liu: Data curation, Formal analysis, Methodology, Writing – original draft. Ziran Yi: Investigation, Data curation. Yunjun Yang:

Investigation, Data curation. **Yatai Li:** Investigation, Data curation. **Jingling Yang:** Conceptualization, Data curation, Methodology, Funding acquisition, Supervision, Writing – review & editing. **Mingshan Zhu:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Data Availability

Data will be made available on request.

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Conflicts of interest

There are no conflicts of interest to declare.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.122788](https://doi.org/10.1016/j.apcatb.2023.122788).

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